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Vitrification of High Level Waste in the UK

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Abstract

In the UK, highly radioactive (HA) liquor from the reprocessing of spent nuclear fuel is converted into a borosilicate glass at the Sellafield Waste Vitrification Plant (WVP) yielding a stable and durable waste form suitable for long-term storage and subsequent disposal. The WVP uses a two-stage design based on the continuous French AVH (Atelier de Vitrification de la Hague) process and as of April 2012 had produced ~2,200 te of waste glass in ~5,600 containers.

WVP product glass is manufactured to a Quality Assured Process Specification, with an historic targeted waste oxide incorporation of 25 wt%. Recently, by using a full-scale inactive test rig to determine operational envelopes, it has been possible for the WVP to implement higher waste loadings. This will result in fewer containers being produced, which will provide considerable savings not only operationally, but also for storage, transport and final disposal.

In addition to changes in Blend ratio and increased waste incorporation, future challenges for the WVP are related to post-operational clean-out (POCO) of the HA liquor storage tanks (HASTs). The waste feed arising from POCO will be enriched in certain species, e.g. molybdenum, which will limit the existing process in terms of waste loading. Hence, work is currently being undertaken to underpin the processing of POCO waste through the WVP.

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1. Introduction

In the UK, reprocessing of spent fuel from the UK's civil nuclear power stations is performed at Sellafield using the PUREX (Plutonium URanium EXtraction) process to recover the uranium and plutonium. The PUREX process, which is based on liquid-liquid solvent extraction using tributyl phosphate (TBP), gives rise to a nitric acid-based liquid waste stream containing the fission products and residual actinides from the spent fuel. This highly active liquor (HAL) is concentrated by evaporation and stored in tanks prior to being converted into a borosilicate glass at the Sellafield Waste Vitrification Plant (WVP). The vitrification process yields a stable and durable waste form suitable for long-term storage and subsequent disposal.

There are two separate reprocessing facilities at Sellafield, i.e.

- the Magnox plant for reprocessing the natural uranium metal based fuel from the UK's first generation Magnox reactors (operational since 1964), and
- THORP (Thermal Oxide Reprocessing Plant) for enriched uranium oxide fuels from AGRs (Advanced Gas Cooled Reactors) and LWRs (Light Water Reactors) (operational since 1994).

As well as the fission products and residual actinides, the HAL waste stream also contains corrosion products, process additives, fuel additives, impurities and residual cladding. The proportions of these groups of elements depend primarily on the type of fuel processed and the reprocessing flowsheet, with additional variations arising from different irradiation and cooling times. Hence, Magnox and THORP (or Oxide) HAL have distinct chemical (and isotopic) compositions. For example, Magnox HAL contains high concentrations of magnesium and aluminium from residual cladding material. However, Oxide HAL contains no Mg or Al, but has elevated fission product and actinide content as well as the presence of gadolinium, which is used as a neutron poison in the process.

The WVP uses a two-stage design based on the continuous French AVH (Atelier de Vitrification de la Hague) process and vitrifies both Magnox and Oxide HAL. However, to ensure that the product from vitrification of Oxide HAL complies with product quality requirements, the Oxide feed has to be blended with Magnox liquor. Currently, the standard blend ratio is 75:25 Oxide:Magnox, although lower ratios, e.g. 50:50, are likely to be implemented in the near future. As of April 2012, WVP had produced ~2,200 te of waste glass in ~5,600 containers.

2. History of HLW Vitrification in the UK

Vitrification as a means of stabilising radioactive waste has been investigated in the UK since the beginnings of the nuclear industry in the 1950s, initially using natural soils as the base materials for glass formulation, see Lutze (1988). However, the high melting temperatures (~1500 °C) required in order to produce homogeneous, bubble-free products led to the development of alternative formulations. Subsequently, lower melting temperature alkali borosilicate glasses that could incorporate up to 40 weight % waste oxides were selected. Table 1 summarises the key stages in the development of UK HLW vitrification.

The early vitrification programmes in the UK focussed on the development of a single-stage 'in-can' batch process based on induction heating, i.e. FINGAL (Fixation in Glass of Active Liquors), see Grover (1966) and HARVEST (Highly Active Residue Vitrification Experimental Studies) in the 1960s and 70s respectively. In parallel, the French were developing a two-stage continuous vitrification process known as AVM (Atelier de Vitrification Marcoule) where the calcination and melting stages were carried out separately, see Clelland (1976).

In 1980, a comparison of the HARVEST and AVM processes concluded that whilst both could be developed to industrial scale, the latter could be implemented more rapidly and had a higher design throughput. Hence, a decision was taken to purchase and implement the AVM process in the UK. A number of aspects of the AVM process that required some development were identified, which resulted in the construction of the Full Scale Inactive Facility (FSIF) at Sellafield in 1981, see Elsden (1988). The FSIF was a full-scale replica of the main features of the AVM plant, which had the main objective of optimising the process for the vitrification of Sellafield-specific wastes.

However, in 1982 the decision was taken to implement the second-generation French AVH (Atelier de Vitrification La Hague) process in the UK's Waste Vitrification Plant (WVP). The larger AVH design had a higher throughput than AVM (25 *vs* 15 kg glass per hour) and used an elliptical rather than cylindrical melter. The design

differences between the AVH-based WVP and the AVM-based FSIF limited the amount of technical underpinning that could be achieved outside the original 25 kg glass per hour at 25 wt% waste incorporation flowsheet, and hence the FSIF was decommissioned in 1991.

The WVP lines 1 and 2 were commissioned in 1989, with the first containers of vitrified HLW being produced in 1990. In order to increase the total throughput, a third line was added in 2002. However, despite the addition of the WVP line 3, there was still a requirement to reduce the stored HAL volumes. To achieve this, improvements in both throughput and waste incorporation on the WVP would be necessary. Hence, in 2001 a second full-scale vitrification research facility; the Vitrification Test Rig (VTR), as described by Bradshaw (2007) was constructed in order to technically underpin the expanded flowsheets.

Table 1. Key stages in the development of HLW vitrification in the UK

Research into vitrification of radioactive waste started	1950s
FINGAL developed at the UK Atomic Energy Authority (AEA) laboratories, Harwell	1960 - 1962
FINGAL operations (72 glass-making runs)	1962 - 1966
Development suspended	1966 -1972
Review decision to continue vitrification development for HARVEST process	1972
Detailed comparison of HARVEST and French AVM process	1979 - 1980
Decision to implement the AVM process for HLW vitrification in the UK	1980
Full scale inactive facility (FSIF) replica of AVM process built	1981 - 1983
Decision that WVP should use the AVH process	1982
FSIF operational	1983 - 1991 (completion of trials in 1989)
Commissioning of WVP Lines 1 and 2	1989 - 1990
WVP Lines 1 and 2 operational	1990 – date
Commissioning of WVP Line 3	1998 - 2002
WVP Line 3 operational	2002 - date
Vitrification Test Rig (VTR) constructed	2002 - 2004
VTR operational	2004 - date

3. WVP Process Description

The two-stage vitrification process used in WVP is shown schematically in Fig. 1. HAL is transferred from the storage tanks to one of four WVP feed tanks, where it is then combined with sugar solution (to reduce ruthenium volatilisation and enhance de-nitration) and fed to an electrically-heated rotary calciner. The calciner evaporates and partially de-nitrates the HAL, producing a dry powder. This ‘calcine’ material is discharged by gravity along with a metered quantity of base glass frit directly into an induction-heated melter crucible and heated to ~1050°C. The calcine reacts with the molten base glass and the resulting homogeneous melt is then periodically poured into product containers. Once filled, the product containers are allowed to cool for at least 24 hours before having a lid welded in place. They are then decontaminated, checked for any activity on the outer surface via swabbing, and then transferred to the Vitrified Product Store (VPS).

The VPS is the interim storage facility for vitrified HLW. It is passively cooled by convection in order to ensure that the glass, which is heated by the radioactive decay, remains well below the glass transition temperature (~500 °C). It consists of 4 storage compartments, each with 199 channels holding up to 10 containers, giving a total capacity of 7960 containers.

The WVP will continue operation until the existing inventory of HAL is immobilized following the planned completion of reprocessing at Sellafield. According to the 2010 UK Radioactive Waste Inventory, it is currently estimated that the WVP will produce ~8,620 containers during its operational lifetime, of which ~1,850 will be returned to overseas customers. This will result in ~6,770 packages containing ~2,700 te of HLW glass for disposal in the UK.

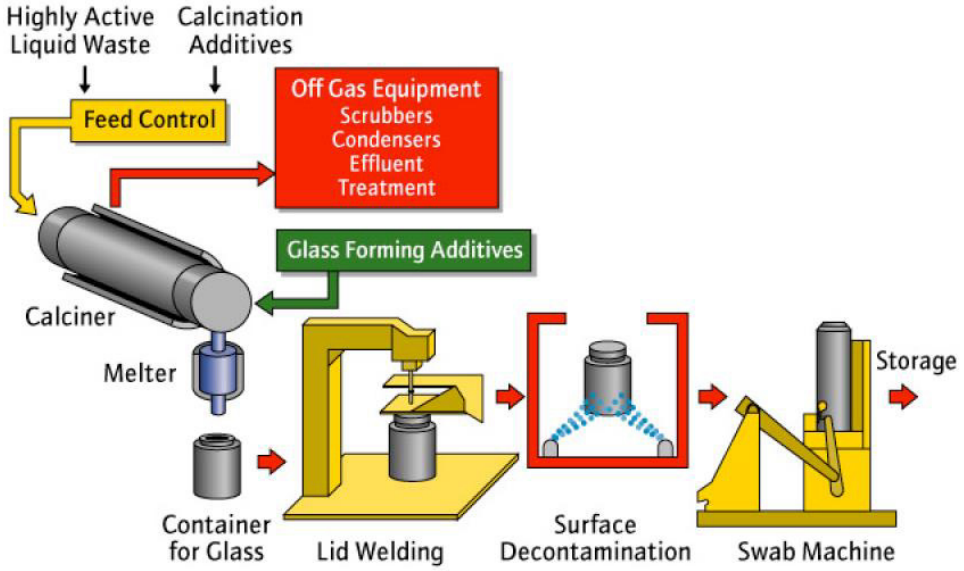

Fig. 1. Schematic of the HLW vitrification process on the Sellafield site

3.1. Development of the Base Glass Used in WVP

Mixed alkali borosilicate glass formulations for the vitrification of HLW were originally developed in the UK for the FINGAL and HARVEST processes in order to maximize the waste incorporation whilst meeting the process requirements (ease of manufacture, melter residence time and viscosity) and having acceptable chemical durability and thermal stability. Following the decision to implement the two-stage AVH process, the 'MW' (Mixture Windscale) composition was selected, which is shown in Table 2.

Table 2. Composition of base glasses used for the vitrification of HLW in the UK

Base Glass Type	SiO_2	B_2O_3	Na_2O	Li_2O
MW	61.75	21.88	11.05	5.33
MW-½Li	63.42	22.50	11.35	2.74

The properties of the 'MW' base glass were found to be optimized with an equimolar amount of Li and Na in the composition. However, it was also found that dosing the HAL with $LiNO_3$ improved the reactivity of the calcine in the melter by suppressing the formation of refractory oxides. The optimum proportions to get the targeted lithia (Li_2O) in 'standard' 25 wt% waste incorporation vitrified product was a 50:50 split between the HAL feed and the base glass. Hence, the 'MW' glass was reformulated with half the Li removed, i.e. 'MW-½Li' in Table 2, which became the standard base glass feedstock. Note that for incorporations other than 25 wt%, because the composition of 'MW-½Li' is fixed, the amount of $LiNO_3$ added to the HAL has to be recalculated in order to maintain equimolar Li and Na in the final product glass.

3.2. Calcination

The calciner consists of a tube (4 m long, 300 mm diameter) inclined at 1.73° (2%) to the horizontal rotating (20 – 30 rpm) inside a four-zone electrical resistance heated furnace at 600 – 840 °C. Fig. 2 shows an image of the calciner used on the full-scale non-active Vitrification Test Rig (VTR). As the HAL flows down the calciner it is

successively dried and de-nitrated; the first two heating zones evaporate the HAL to dryness forming solid waste nitrates, and the second two partially de-nitrate the solids forming a waste oxide calcine, as shown in Fig. 2.

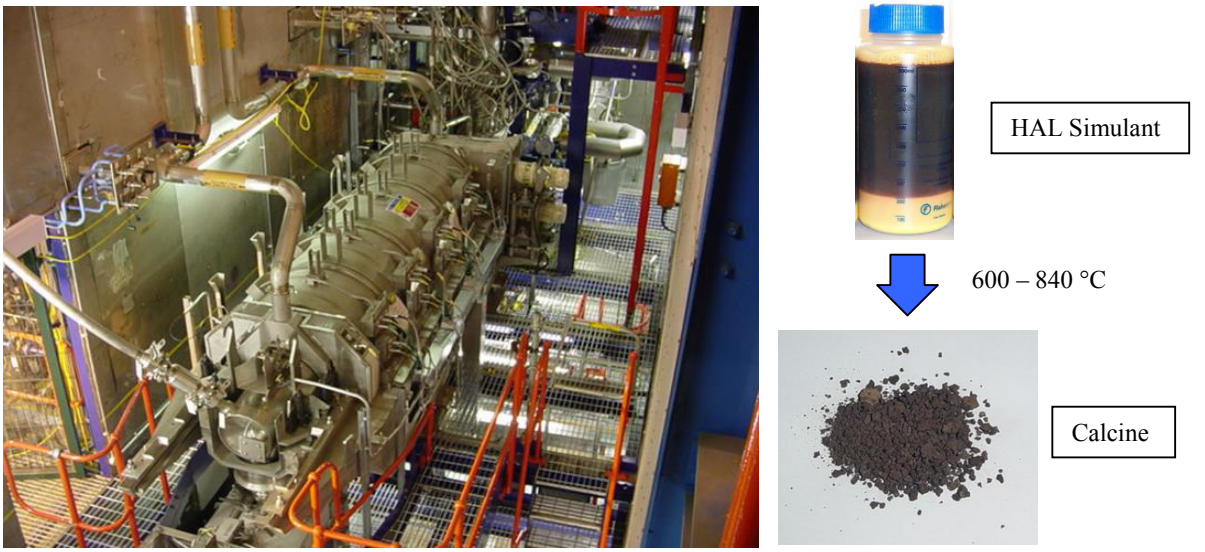

Fig. 2. Full-scale calciner on the non-active Vitrification Test Rig (VTR) showing conversion of HAL simulant to calcine material.

3.3. Melting and Pouring

The melting stage of the WVP process is designed to produce a homogenous and reproducible glass product. This is achieved by heating a mixture of MW-½Li base glass frit and calcine in an elliptical Nicrofer® 6025 HT alloy melter crucible (working volume ~100 litres) using electrical induction. Frit and calcine are fed over an 8 hour period with mixing provided by four argon or air sparge tubes. The glass is then poured into the product container once the temperature is >1000 °C (typically 1050 °C) through an induction-heated freeze valve. Each pour is ~200 kg glass, with ~70 kg remaining in the crucible as a heel.

The Vitrification Product Container (VPC) is a 169 litre capacity cylindrical 309 stainless steel vessel. This is sufficient for two ~200 kg pours giving a total of ~400 kg glass per container.

4. WVP Product Quality

Vitrified product fabricated by the WVP is not sampled, instead the process is qualified. That is, the approach to ensuring product quality is to control the production process within the bounds of the 'HLWP Process Specification'. In particular, control of the composition and properties of the vitrified residue is achieved by sampling and analysis of HAL prior to feeding, control of the base glass feedstock and other additives, and careful control of calciner and melter process conditions. The rigorous approach to process control and feed analysis ensures that the final product does not require routine sampling as part of the quality assurance process.

Development work with inactive simulants at laboratory and rig scale has been used to determine the envelope of feed chemistry and process operating conditions that yields good product quality. During WVP operation, records are kept to show that the process remained within these constraints, which are managed using limits set out in the 'HLWP Process Specification'.

4.1. Underpinning R&D

A large amount of underpinning R&D exists for vitrification of UK HLW, dating from the early development work at the Harwell Laboratories in the 1950s. Historic studies included R&D on active feeds; actual HAL from the

lab-scale reprocessing of AGR fuel was vitrified, as well as doped 'source term' samples containing some specific long-lived radionuclides such as Tc, Np and Pu.

The WVP development programme itself consisted of an extensive series of laboratory trials with a wide range of waste types and incorporations. Full scale trials were carried out on the FSIF, which, with the actual commissioning of the three WVP lines, demonstrated the baseline flowsheet of 25 wt% Magnox and 75:25 Blend product at a throughput of 25 kg/hr.

More recently, the VTR has demonstrated expanded flowsheets by underpinning the vitrification of higher waste incorporations (up to 35 wt%), higher throughputs (up to ~33 kg/hr), and wider feed envelopes (50:50 Blends, etc.). The VTR has also been successful in demonstrating the product quality of containers produced with small deviations from the 'HLWP Process Specification', e.g. calciner tube rotations as low as 15 rpm. The current challenge for the VTR is to demonstrate the vitrification of HAL feeds resulting from the Post Operational Clean Out (POCO) of the HAL storage tanks. These feeds, which are expected to be enriched with settled solids such as zirconium molybdate, are not currently included in the 'HLWP Process Specification' and therefore need to be technically underpinned by full scale inactive trials.

4.2. Assessment of Product Quality

The product quality of the glasses produced during the various HLW vitrification R&D programmes is demonstrated to be within acceptable limits via a standard set of laboratory assessments. These include a visual inspection for undissolved phases, bubbles, cracks, etc. using a systematic scoring system, SEM to measure the quantity and identify the undissolved phases, density, viscosity, glass transition temperature, heat treatments to test the thermal stability, and various leach tests to demonstrate acceptable aqueous durability.

5. Summary

Vitrification of HLW has been studied in the UK since the early days of the nuclear industry in the 1950s. This work culminated in the commissioning of WVP lines 1 and 2 at Sellafield in 1990, with a third line added in 2002. The WVP uses the French two-stage calcination-melting AVH process with a baseline throughput and waste incorporation of 25 kg/hr and 25 wt% respectively. To date, nearly 6,000 containers and 2,500 te HLW glass have been produced and are currently stored pending final deep geological disposal. Recent R&D programs combining laboratory and full scale studies on the VTR have demonstrated expanded flowsheets, with increased waste incorporations up to 32 wt% now implemented on WVP.

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